

Triennial changes in groundwater quality in aquifers used for public supply in California: utility as indicators of temporal trends

Robert Kent  · Matthew K. Landon

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Abstract From 2004 to 2011, the U.S. Geological Survey collected samples from 1686 wells across the State of California as part of the California State Water Resources Control Board's Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project (PBP). From 2007 to 2013, 224 of these wells were resampled to assess temporal trends in water quality. The samples were analyzed for 216 water-quality constituents, including inorganic and organic compounds as well as isotopic tracers. The resampled wells were grouped into five hydrogeologic zones. A non-parametric hypothesis test was used to test the differences between initial sampling and resampling results to evaluate possible step trends in water-quality, statewide, and within each hydrogeologic zone. The hypothesis tests were performed on the 79 constituents that were detected in more than 5 % of the samples collected during either sampling period in at least one hydrogeologic zone. Step trends were detected for 17 constituents. Increasing trends were detected for alkalinity, aluminum, beryllium, boron, lithium, orthophosphate, perchlorate, sodium, and specific conductance. Decreasing trends were detected for atrazine, cobalt, dissolved oxygen, lead, nickel, pH, simazine, and

tritium. Tritium was expected to decrease due to decreasing values in precipitation, and the detection of decreases indicates that the method is capable of resolving temporal trends.

Keywords California groundwater · Trend analysis · Water-quality monitoring · Public supply wells

Introduction

Temporal trends of groundwater quality are difficult to assess due to the long time scales involved with groundwater movement and the resulting changes in quality, although relatively short-term studies have been used to monitor the progress of remediation efforts (McHugh et al. 2014; Stoline et al. 1993). Groundwater-quality trend studies often focus on only one or two water-quality constituents (Hantzsche and Finnemore 1992; Batlle Aguilar et al. 2007; Burow et al. 2007; Landon et al. 2011; Kent and Landon 2013), and relatively few studies have evaluated temporal trends for three or more water-quality constituents (Stoline et al. 1993; Barlow et al. 2012; Lindsey and Rupert 2012). However, it is desirable to concurrently assess trends in a large suite of constituents to develop a comprehensive understanding of trends in groundwater quality. An understanding of whether concentrations of water-quality constituents are generally increasing, decreasing, or remaining constant over time would help water resource managers plan for the future.

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R. Kent (✉) · M. K. Landon
U.S. Geological Survey California Water Science Center, 4165
Spruance Road, Suite 200, San Diego, CA 95101-0812, USA
e-mail: rhkent@usgs.gov

There have been several studies describing water-quality trend analysis methods (Hirsch et al. 1991; Loftis 1996; Grath et al. 2001; Wahlin and Grimvall 2010; Lopez et al. 2014), as well as studies that estimate the ability of these methods to assess and predict future groundwater quality (Hantzsche and Finnemore 1992; Stuart et al. 2007; Visser et al. 2009). Some trend evaluation studies are purely descriptive, involving neither formal hypothesis testing nor quantification, but include graphical methods and summary statistics (Bodo 1989; Esterby 1996). However, most studies that evaluate temporal trends in water quality use one of two statistical modes (Hirsch et al. 1991). The first mode performs correlation tests on data time-series where time is the independent variable, and some measure of water quality is the dependent variable (Stoline et al. 1993; Batlle Aguilar et al. 2007; Landon et al. 2011; Kent and Landon 2013; Chaudhuri and Ale 2014). Changes detected by this mode are sometimes referred to as *monotonic trends* (Hirsch et al. 1991; Esterby 1996); the European Water Framework Directive recommends at least eight measurements when using this mode of trend analysis (Grath et al. 2001). The second statistical mode performs hypothesis tests on the differences between two or more sets of water-quality data collected at distinct time periods (Burow et al. 2008; Rupert 2008; Saad 2008; Barlow et al. 2012; Lindsey and Rupert 2012). Changes detected by this mode are sometimes referred to as *step trends* and are more likely to be detected if there is a relatively long gap between the time periods (Hirsch et al. 1991). The present paper summarizes the analysis of trends over approximately 3-year periods without exploring, in detail, the causes of such trends.

California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project

The California State Water Resources Control Board implemented the Groundwater Ambient Monitoring and Assessment (GAMA) program to assess California groundwater quality (GAMA, <http://www.waterboards.ca.gov/gama/>). The GAMA Priority Basin Project (GAMA-PBP) is a part, conducted in cooperation with the U.S. Geological Survey (USGS) (<http://ca.water.usgs.gov/gama/>; Kulongoski and Belitz 2004). GAMA-PBP is conducting three types of water-quality assessments: (1) status of groundwater quality, (2) understanding of factors that affect groundwater quality,

and (3) trends in groundwater quality. The present study investigated step trends in the concentrations of 216 water-quality constituents over approximately 3-year time periods on a regional scale using a consistently collected groundwater quality dataset spanning major hydrogeologic provinces of California (Belitz et al. 2003).

The statewide assessment was conducted by sequentially sampling 34 defined “study units” ranging in area from less than 80 km² (Santa Barbara study unit) to more than 40,000 km² (Sierra Nevada study unit) (Online Resource 1). Groundwater-quality assessments are facilitated by grouping study units into regions with relatively similar geologic, climatic, and hydrologic characteristics. Belitz et al. (2003) defined 10 hydrogeologic provinces in their framework report which established the design of the GAMA-PBP. For the present trend, evaluation study units were grouped into five condensed hydrogeologic zones—Central Valley, Coastal, Desert, Mountain, and Southern California—so that each zone would have enough samples for robust statistical testing (Table 1; Fig. 1).

Methods

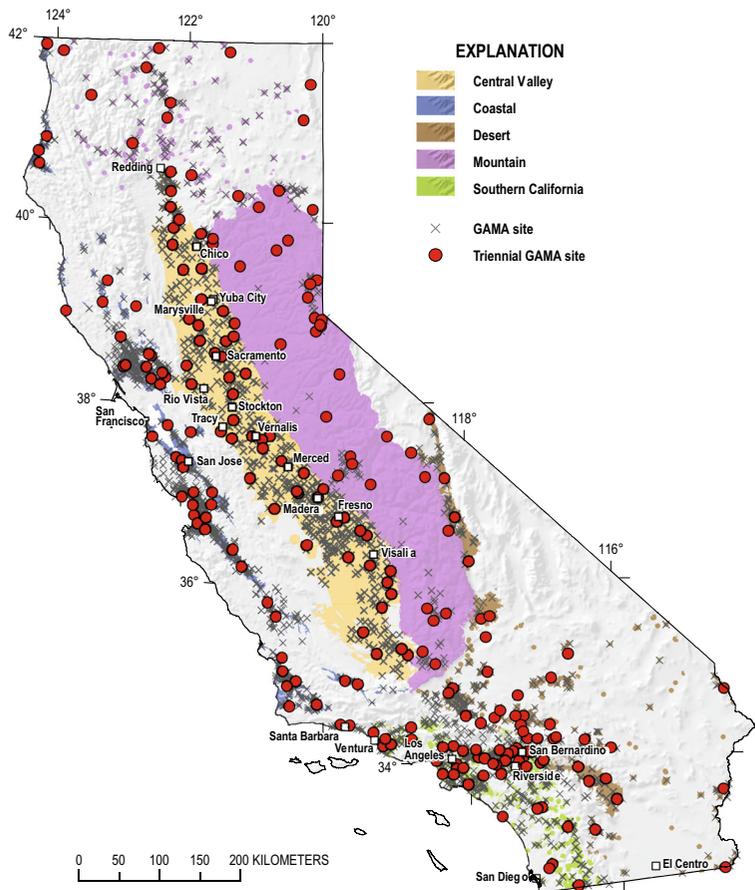
Status well selection

The initial sampling was designed to provide a spatially unbiased status assessment of the quality of untreated groundwater used for public water supplies in California. Study areas were the fundamental unit of organization for the GAMA-PBP. In alluvial basins with broadly distributed public supply wells, the entire basin was defined as a study area and represented by a grid of equal-area cells. In basins that contain relatively large

Table 1 Summary information on hydrogeologic zones and their groupings for triennial trend evaluations

Hydrogeologic zone	Assessed area (km ²)	Number of status wells	Number of trend wells
Desert	7607	249	32
Mountains	21,707	289	50
Coastal	8952	384	47
Southern California	9803	275	43
Central Valley	39,238	489	52
Grand total	87,307	1686	224

Fig. 1 Map of California showing hydrogeologic zones, trend wells, and status wells not re-sampled for trends



areas without wells, and in hard-rock areas, a “buffered” approach was used (Belitz et al. 2010). In the buffered approach, the study area was defined as the collective area within 3 km of any given public supply well; the collective area was then represented by a grid of equal-area cells. The GAMA-PBP assessed 87 study areas defined in this manner, which included nearly all of the groundwater used statewide for public drinking-water supply (Belitz et al. 2015). Eighty-three of the 87 study areas were included in the present assessment of trends. During initial sampling for the status assessment, the 83 study areas were divided into a total of 2037 cells.

Wells from the California Department of Public Health (CDPH) database were assigned random ranks, and the highest ranked well in each grid cell that met basic sampling criteria and for which permission to be sampled could be obtained was sampled. For some cells having no available CDPH wells, an irrigation or a domestic well having a perforation interval similar to

that of CDPH wells in the area was sampled. Some cells contained no wells that were both appropriate for sampling and accessible. Therefore, not all 2037 cells could be included in the status assessment. From 2004 to 2011, the GAMA PBP collected samples from 1686 wells selected in this manner in the 83 study areas evaluated for trends. The GAMA PBP program refers to these wells as “status wells.” Additional details on selection of wells and the grid design for each study unit can be found in USGS Reports for each study unit accessible from the “Publications” link at: <http://ca.water.usgs.gov/projects/gama/>.

Trend well selection

Approximately 3 years after their respective initial sampling, a subset of the 1686 status wells were selected for resampling as “trend wells” by randomly ranking the status wells in each study area and then sampling the highest ranked wells that remained available for

sampling. At least 10 % of the status wells in each study area were resampled, and more than 10 % were resampled in a few study units for various reasons (Kent et al. 2014, Kent 2015). For example, the number of trend wells was rounded up in each study area so that if a study area had 21 status wells, typically three of these would be selected as trend wells. From September 2007 to December 2013, the GAMA PBP collected samples from 224 trend wells. Sample dates for the trend wells, as well as attributes including elevation, construction information, land use, age classification, and geologic category are provided in Online Resource 2. For these trend wells, the time difference between the initial sample and resampling had a median of 3.01 years and ranged from 1.94 to 4.94 years. Trend wells in this study are primarily used for public supply, which are typically drilled deeper than are wells used for domestic or small-community supply (U.S. Geological Survey 2013). Trend wells (excluding 11 springs sampled in the Mountain hydrogeologic zone) were drilled to a median depth of 131 m (Online Resource 2).

Data acquisition

Groundwater samples for the GAMA-PBP are collected using consistent protocols designed to minimize inadvertent sample contamination (Koterba et al. 1995; U.S. Geological Survey 2006). Detailed descriptions of sample collection and analysis methods can be found in USGS GAMA PBP Data Series Reports accessible from the “Publications” link at: <http://ca.water.usgs.gov/projects/gama/>. Trend samples were analyzed for 216 water-quality constituents, including nutrients, major ions, trace elements, perchlorate, pesticides, volatile organic compounds, and isotopic tracers (Online Resource 3). Analyses for nutrients, major ions, trace metals, pesticides, and volatile organic compounds were performed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Analyses for perchlorate were performed by Montgomery Watson Harza Laboratories in Monrovia, California, prior to October 2007, and by Weck Laboratories, Inc. in City of Industry, California, as of October 2007. Analyses for carbon isotopes were performed by the University of Arizona, Accelerator Mass Spectrometry Laboratory in Tucson, Arizona prior to 2005, by the Environmental Isotope Laboratory, University of Waterloo from 2005 until 2010, and to the Woods Hole Oceanographic Institution, National Ocean

Sciences Accelerator Mass Spectrometry Facility in Woods Hole, Massachusetts as of 2010. Analysis for tritium was performed by the USGS Isotope Tracers Laboratory in Menlo Park, California. Analyses of the stable isotopes of oxygen and hydrogen of water were performed by the USGS Reston Stable Isotope Laboratory in Reston, Virginia.

Statistical methods for the determination of trends

Statistical procedures were used to evaluate whether the concentrations (or activities) of individual constituents might be increasing or decreasing in groundwater within each of the five hydrogeologic zones. Evaluations were performed for all constituents that were detected in at least 5 % of trend well samples collected during initial sampling or resampling. Constituents detected in fewer than 5 % of the samples were unlikely to have sufficient data for detecting step trends. The data were organized by hydrogeologic zone, and initial and resampling results for each constituent meeting the 5 % detection frequency criterion were paired up well-by-well.

A threshold difference between results of the initial sampling and resampling was set so that small differences due to analytical variability would not support a conclusion that a trend was occurring. Analytical variability can be evaluated by submitting duplicate samples to a laboratory (replicates) and comparing the duplicate results. Project objectives define criteria to determine whether or not the results for the replicate samples are similar enough to be acceptable.

The method for setting the threshold difference between initial sampling and resampling results was based on methods used by the GAMA-PBP to determine whether or not replicate results are acceptable (Kent et al. 2014, p. 148). If two results are similar enough to constitute a replicate that is acceptable for project objectives, the small difference between them should not support the conclusion that a trend is occurring. GAMA-PBP replicate results are considered acceptable (not different) for low constituent concentrations if the standard deviation for the replicate pair is less than one half of the reporting limit at the time of analysis. For purposes of this evaluation, a low concentration is less than five times the reporting limit. For concentrations greater than five times the reporting limit, replicate results are acceptable if the relative standard deviation (also known as the coefficient of variation) for the replicate pair is less than 10 %. When the difference

between paired sampling results did not exceed the applicable threshold for the water-quality constituent in question, the two sample results were considered analytically identical and each result was substituted with the sample pair mean so that a zero difference was indicated for that sample for the purpose of group tests on differences.

Threshold differences were calculated as described above for all of the evaluated water-quality constituents except for pH, carbon-14 (in percent modern carbon), and the isotopic ratios of hydrogen and oxygen in water. The concepts of detection level and reporting limit are not relevant for the measurements of pH, carbon-14, or the isotopic ratios of hydrogen and oxygen in natural water. The manufacturer of the field meters used by the GAMA-PBP for the measurement of pH specifies a precision of ± 0.2 standard pH units (<http://www.ysi.com/productsdetail.php?556MPS-21>). Since this level of precision implies that it would be possible for one of the two paired results to be as much as 0.2 units greater than the true value, and the other to be as much as 0.2 units less than the true value, the threshold difference used for both field and laboratory-measured pH was 0.4 standard pH units. The three laboratories that performed analyses of carbon isotopes provided estimates of counting error in their measurements of carbon-14. Therefore, the threshold difference for carbon-14 pairs was the greatest estimated error for the two results of percent modern carbon. No estimated error nor uncertainty is provided by the Reston Stable Isotope Laboratory with their isotopic ratios of hydrogen and oxygen in water. Therefore, the threshold difference between initial sampling and resampling results for these isotopic ratios was a relative standard deviation greater than or equal to 10 %.

Trend samples for this study were collected and submitted to laboratories approximately 3 years later than were the initial GAMA-PBP samples. Between sampling periods, reporting levels changed for many of the constituents. When the reporting level for the initial sample was different from that for the trend sample, the greater of the two reporting levels was applied for the purpose of determining the threshold. When a laboratory does not detect a constituent in a sample, the result is censored and expressed as less than (<) the reporting level. In cases where the result for one of the two samples from a well was censored, and the other uncensored (detected), the censored result was substituted with the reporting level in effect at the time of

analysis so that the measured difference between the censored and uncensored results was the minimum difference possible. For example, if the result for one of the two samples was 5 mg/L and the result for the other was <1 mg/L, the difference between these sample results would be calculated as 4 mg/L, even though the difference could be as great as 5 mg/L if the constituent was totally absent in the sample with the censored result. Additionally, in such cases where the uncensored (detected) result was less than the reporting level of the censored result, the results were considered analytically identical and each result was substituted with the reporting level of the censored result. This conservative approach was used to avoid overestimating observed changes while performing the tests on differences.

The GAMA-PBP has periodically evaluated the occurrence of constituents detected in project blank samples to define threshold concentrations above which one can be reasonably certain that detections in groundwater samples are not the result of contamination (Olsen et al. 2010; Fram et al. 2012; Davis et al. 2014). Based on such threshold concentrations, the program establishes study reporting levels (SRLs), which are used to censor results at concentrations that are sometimes greater than the laboratory reporting levels. Results at concentrations less than an established SRL are published in GAMA-PBP reports as \leq the concentration reported by the laboratory. Results censored by SRLs in effect during the collection of data used in the present study were treated the same as results censored by laboratory reporting levels.

After processing the data in this way, a Wilcoxon signed-rank test with a modification proposed by Pratt (1959) was performed comparing the paired results (initial and trend sampling results), statewide and within each hydrogeologic zone, for each evaluated constituent to determine whether or not the concentration of the constituent was increasing or decreasing in a statistically significant way. The Wilcoxon signed-rank test is a nonparametric alternative to a paired *t* test that does not assume that the data have a normal distribution, an assumption often violated with water-quality data (Helsel and Hirsch 2002). It is used to test whether the median difference between paired observations equals zero (null hypothesis). The absolute values of the differences are ranked, so that the relative magnitudes and the relative number of changes in each direction (increases or decreases) are both taken into account. When there is no difference between paired results, the

traditional Wilcoxon signed-rank test discards that pair before the evaluation. Data used for the present study include many pairs with zero differences, due to a prevalence of non-detections, and the imposed requirement that differences between the paired results exceed the previously-defined thresholds. The Wilcoxon signed-rank test with the modification proposed by Pratt (1959) was preferred for this study, because it ranks all of the differences, including the zero differences, although it only uses the non-zero differences to calculate a p value. A trend was considered detected at a significance level $\geq 95\%$ (attained significance level $p = 0.05$).

Statistical methods to evaluate potential explanatory factors

Statistical procedures were used to evaluate whether or not there were relationships among the three constituent change categories (unchanged, increases, decreases greater than the threshold difference) and continuous well attribute variables. The continuous well attribute variables were total well depth, depth to the top of the highest perforation, land use percentages (agricultural, natural, and urban), and classified groundwater age based on activities of the radioisotopes tritium and carbon-14. Kruskal-Wallis rank-sum tests were performed to determine whether or not there were statistically significant differences for the continuous well attribute variables among the three constituent categories. The Kruskal-Wallis rank-sum test is a nonparametric alternative to a one-way analysis of variance (Helsel and Hirsch 2002). In addition, Wilcoxon rank-sum tests were performed to more specifically determine whether or not there were statistically significant differences for the continuous well attribute variables between the increasing and decreasing categories. The Wilcoxon rank-sum test is a nonparametric alternative to a two-sample t test (Helsel and Hirsch 2002).

Results

Seventy-nine of the 216 analyzed constituents were detected in at least 5 % of the samples collected in one or more of the hydrogeologic zones during initial sampling or resampling of trend wells (Online Resource 3). These 79 constituents included eight pesticides or pesticide degradates, 20 volatile organic compounds,

perchlorate, seven water-quality indicators (including total dissolved solids, alkalinity, and hardness), nine major or minor ions, silica, five nutrient (nitrogen or phosphorus) species, 24 trace elements, and four isotopic tracers. All of these 79 constituents were evaluated for possible temporal step trends by hydrogeologic zone and on a statewide basis. The number of results available for both samples collected from the 224 trend wells varied by constituent and by hydrogeologic zone (Table 2, Online Resource 4), generally because not all constituents were collected at all sites in the initial sampling. This is important to note, because the ability for a statistical test to detect a difference (when it exists) improves with increasing sample size (Anderson 1987).

For most of the 79 evaluated constituents, the Wilcoxon signed-rank test with Pratt modification found no conclusive evidence of step trends between sampling periods in any of the hydrogeologic zones. Results of statistical evaluations for the 62 constituents with no evidence of step trends are provided in Online Resource 4. Statistically significant step trends were detected for 17 water-quality constituents in one or more of the hydrogeologic zones: tritium, orthophosphate, perchlorate, dissolved oxygen, specific conductance, pH, alkalinity, sodium, aluminum, beryllium, boron, cobalt, lead, lithium, nickel, atrazine, and simazine (Table 2). Figures 2, 3, and 4 are scatterplots of the initial vs. trend sampling results for tritium, orthophosphate, and perchlorate. Figure 5 is a map showing perchlorate results of paired trend sampling throughout California. Figures 6 and 7 are scatterplots of the initial and trend results for pH and atrazine (scatterplots and maps for the other constituents exhibiting step trends are provided in Online Resource 5). On the scatterplots, paired-sample results with differences exceeding the difference threshold are represented by symbols representing the hydrogeologic zone of the wells involved. Paired-sample results with differences less than the difference threshold are represented by gray symbols. Summary statistics of the magnitudes of change for the 17 constituents exhibiting trends are provided in Online Resource 6.

The statistical procedures used to evaluate the constituents with step trends for relationships among the three constituent change categories for trend wells (unchanged, increases, decreases greater than the threshold difference) and continuous well attribute variables revealed little about the evaluated potential explanatory factors. In several cases, the Kruskal-Wallis test showed

Table 2 Trend evaluation, statewide and by hydrogeologic zone, on constituents for which at least one step trend was observed

Constituent	Statewide			Central Valley			Southern California					
	Number of wells	Increase ^a	Decrease ^a	Number of wells	Increase ^a	Decrease ^a	Number of wells	Increase ^a	Decrease ^a			
Tritium	190	14	49	<0.001 –	37	5	14	0.022 –	28	0	8	0.005 –
Orthophosphate	139	31	12	0.002 +	27	8	0	0.005 +	17	4	0	0.046 +
Perchlorate	198	17	7	0.036 +	45	4	1	0.167	40	8	1	0.016 +
Dissolved oxygen	195	45	49	0.520	42	5	13	0.039 –	35	8	10	0.820
Specific conductance	224	11	5	0.137	52	2	1	0.579	43	5	0	0.025 +
pH	166	1	10	0.007 –	27	1	1	0.979	29	0	0	NA
Alkalinity	136	8	0	0.005 +	29	3	0	0.083	18	0	0	NA
Sodium	133	7	1	0.032 +	29	2	1	0.536	18	2	0	0.157
Aluminum	133	12	4	0.043 +	29	4	0	0.046 +	18	1	0	0.317
Beryllium	133	7	0	0.008 +	29	3	0	0.083	18	0	0	NA
Boron	133	17	9	0.135	29	6	0	0.015 +	18	2	2	0.952
Cobalt	28	9	11	0.695	9	0	4	0.048 –	15	9	4	0.221
Lead	133	6	18	0.016 –	29	1	6	0.052	18	2	1	0.519
Lithium	133	15	9	0.210	29	2	3	0.679	18	2	3	0.578
Nickel	133	14	31	0.014 –	29	2	9	0.032 –	18	8	5	0.627
Atrazine	218	1	8	0.020 –	51	0	0	NA	42	1	8	0.022 –
Simazine	218	3	5	0.481	51	2	0	0.157	42	0	5	0.025 –
Constituent												
	Desert			Mountain				Coastal				
	Number of wells	Increase ^a	Decrease ^a	Number of wells	Increase ^a	Decrease ^a	Number of wells	Increase ^a	Decrease ^a	Number of wells	Increase ^a	Decrease ^a
Tritium	32	1	3	0.294	46	4	12	0.027 –	47	4	12	0.038 –
Orthophosphate	19	8	0	0.005 +	46	4	8	0.280	30	7	4	0.332
Perchlorate	32	1	2	0.539	45	0	2	0.157	36	4	1	0.172
Dissolved oxygen	32	8	3	0.202	48	13	13	0.527	38	11	10	0.532
Specific conductance	32	1	1	0.982	50	1	1	0.989	47	2	2	0.982
pH	32	0	1	0.317	45	0	7	0.008 –	33	0	1	0.317
Alkalinity	20	1	0	0.317	46	3	0	0.083	23	1	0	0.317
Sodium	19	1	0	0.317	46	2	0	0.157	21	0	0	NA
Aluminum	19	2	1	0.564	46	4	2	0.404	21	1	1	0.972
Beryllium	19	1	0	0.317	46	2	0	0.157	21	1	0	0.317
Boron	19	2	3	0.656	46	4	3	0.745	21	3	1	0.306
Cobalt	0	0	0	NA	1	0	0	NA	3	0	3	0.109

Table 2 (continued)

Lead	19	0	4	46	2	4	0.404	21	1	3	0.357
Lithium	19	1	2	46	8	1	0.017 +	21	2	0	0.157
Nickel	19	0	3	46	2	9	0.035 -	21	2	5	0.243
Atrazine	30	0	0	NA	0	0	NA	46	0	0	NA
Simazine	30	1	0	49	0	0	NA	46	0	0	NA

^a Observed increases (+) or decreases (-) greater than the threshold difference established by this study

^b Significance attained on 2-sided Wilcoxon signed-rank test (zero method = Pratt) on differences between initial and resample paired results. *P* values less than 0.05 are in bold font

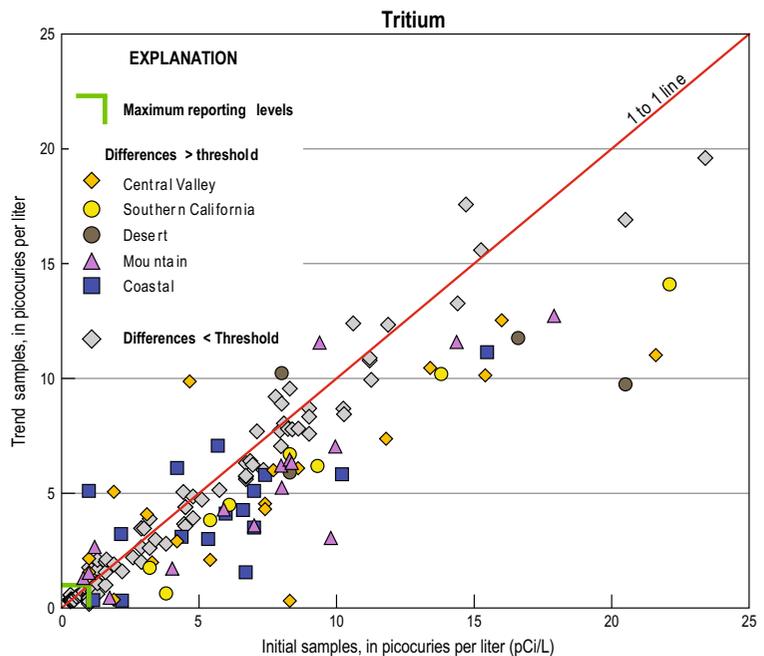
significant differences among all three categories, but the Wilcoxon rank-sum tests, which looked specifically for differences between the increasing and decreasing groups, did not show significant results. Orthophosphate was a notable exception. The Kruskal-Wallis test results suggested that well depths and depths to the top perforation were significantly different among the change categories. Moreover, the Wilcoxon rank-sum test results more specifically suggested that wells for which orthophosphate increased were more likely to have deeper total depths and depths to the top perforation than did wells for which orthophosphate decreased. Wilcoxon rank-sum test results also suggested a relationship between urban land use and increases in orthophosphate concentrations. Kruskal-Wallis and Wilcoxon rank-sum test results for the statewide data sets, along with the median values for each change category, are provided for the 17 constituents with step trends in Online Resource 7.

Discussion

Temporal trends in groundwater quality cannot be detected in individual wells by comparing results from just two samples collected only 3 years apart. In this study, logically grouping the results by regions sharing relatively similar geologic, climatic, and hydrologic characteristics provided statistical mass, which allowed the detection of step trends for 17 water-quality constituents in one or more hydrogeologic zones. The hypothesis tests did not indicate step trends for 62 other constituents with sufficient detection frequencies to merit evaluation. It should be noted, it cannot be concluded from failure to reject the null hypothesis of no difference in a temporal step trend test that observed changes in groundwater quality are random. A larger number of comparisons or a greater time interval may reveal significant temporal trends not evident with the data that are currently available.

Tritium showed the most convincing evidence of temporal step trends in this study. Tritium activities decreased statewide and in four of the five hydrogeologic zones. Even in the Desert hydrogeologic zone, where step trends were not detected, the number of decreases with a magnitude greater than the threshold difference used in this study exceeded the number of such increases. Decreases in groundwater tritium activity might be expected in all zones based upon slowly

Fig. 2 Scatterplot of tritium activities measured in initial vs. trend samples



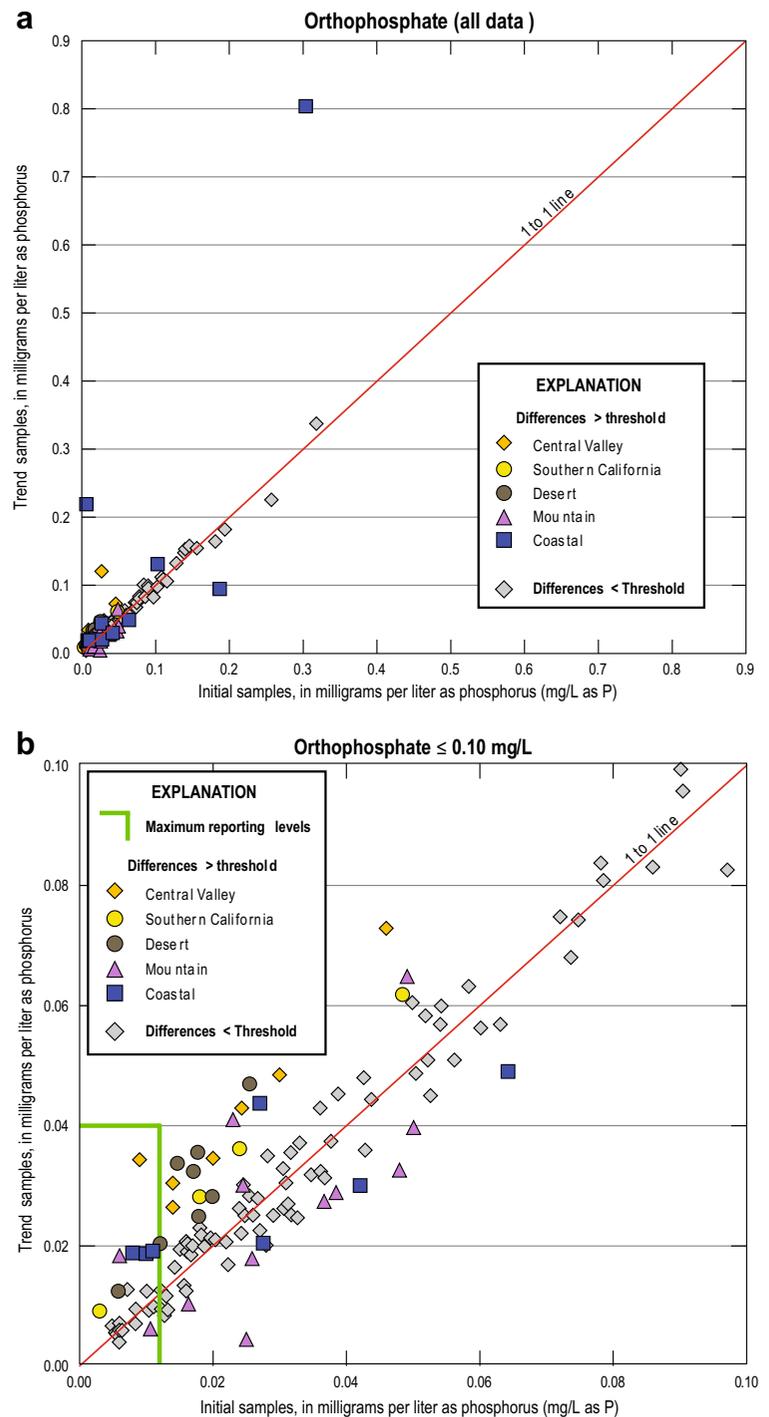
declining tritium activity in precipitation, as the effects of atmospheric nuclear testing in the 1950s and 1960s diminish and due to radioactive decay (Stewart et al. 2010). Tritium is an unstable (radioactive) isotope of hydrogen, with a half-life of approximately 12.3 years (Plummer et al. 1993). Expected tritium activities for trend samples based on radioactive decay alone were calculated for the 132 wells in which tritium was detected in the initial sample. The average expected (calculated) change in tritium activity for these wells was a decrease with a median of 1.04 (mean = 1.19 pCi/L). The average observed change in tritium activity for these wells was a decrease with a median of 0.75 (mean = 1.17) pCi/L. So, while a finding of decreasing tritium may not be unexpected, the ability to systematically detect the decrease demonstrates that the trend evaluation method is capable of detecting change.

Phosphate, including ortho-, pyro-, and polyphosphates is the only significant form of dissolved phosphorus in natural water (Hem 1992). In unpolluted fresh waters, phosphate is normally the limiting nutrient for aquatic plant growth (Drever 1997), so its presence in groundwater is most relevant where there are surface-water interactions. Consequently, increases in phosphate can result in substantial changes in algal activity, sometimes culminating in harmful algal blooms (Mueller et al. 1995). Orthophosphate increased statewide, as well

as in the Central Valley, Southern California, and Desert hydrogeologic zones. While there are some uncertainties in the analyses of orthophosphate that warrant further discussion (Online Resource 8), these were unlikely to have altered the results of the step trend analysis described above.

Orthophosphate can enter surface water, and subsequently groundwater, from chemical phosphorus fertilizer (Domagalski and Johnson 2012), manure application (Gianessi and Peskin 1984), or detergents containing phosphates (Hammond 1971). Around 1994, the household laundry detergent industry voluntarily ended the manufacture of phosphate detergent, at a time when applications of chemical fertilizers and manure were already starting to be controlled (Litke 1999). The Kruskal-Wallis and Wilcoxon rank-sum test results (Online Resource 7) indicated that wells in which the groundwater was increasing in orthophosphate had significantly deeper top perforation and total depths than did wells in which the groundwater was decreasing or unchanging. These statistical test results support a hypothesis that deeper wells are more likely to contain groundwater recharged before phosphorus controls went into effect. Although classified groundwater age, as indicated by tritium and carbon-14 activity, was not related to orthophosphate trend categories, these age-tracer data generally cannot be used to distinguish

Fig. 3 Scatterplots of orthophosphate concentrations measured in initial vs. trend samples. **a** All data. **b** Concentrations ≤ 0.10 mg per liter as P



pre-and post 1990s recharge. The statistical test results (Online Resource 7) also suggested that groundwater in wells with increasing orthophosphate are more likely to have a higher percentage of urban land use and a lower percentage of natural land use around

them than are wells in which groundwater orthophosphate is decreasing or unchanging.

The observed increasing perchlorate step trend primarily reflects increases in wells where sample concentrations are >1 $\mu\text{g/L}$ (Fig. 4a, b). At concentrations

Fig. 4 Scatterplot of perchlorate concentrations measured in initial vs. trend samples

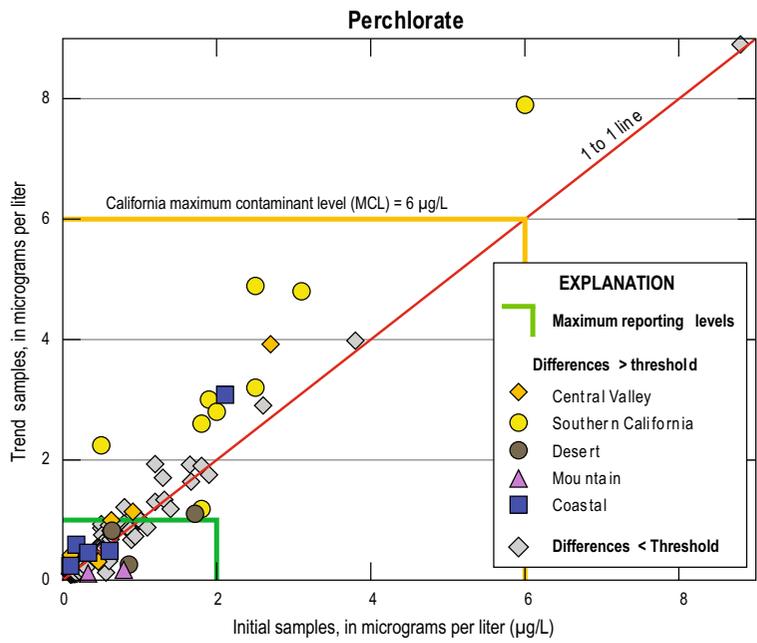


Fig. 5 Map of California showing wells with paired data for perchlorate. Symbol legend: orange upward triangles = perchlorate increase > threshold difference, green downward triangles = perchlorate decrease > threshold difference, white circles = difference < threshold difference

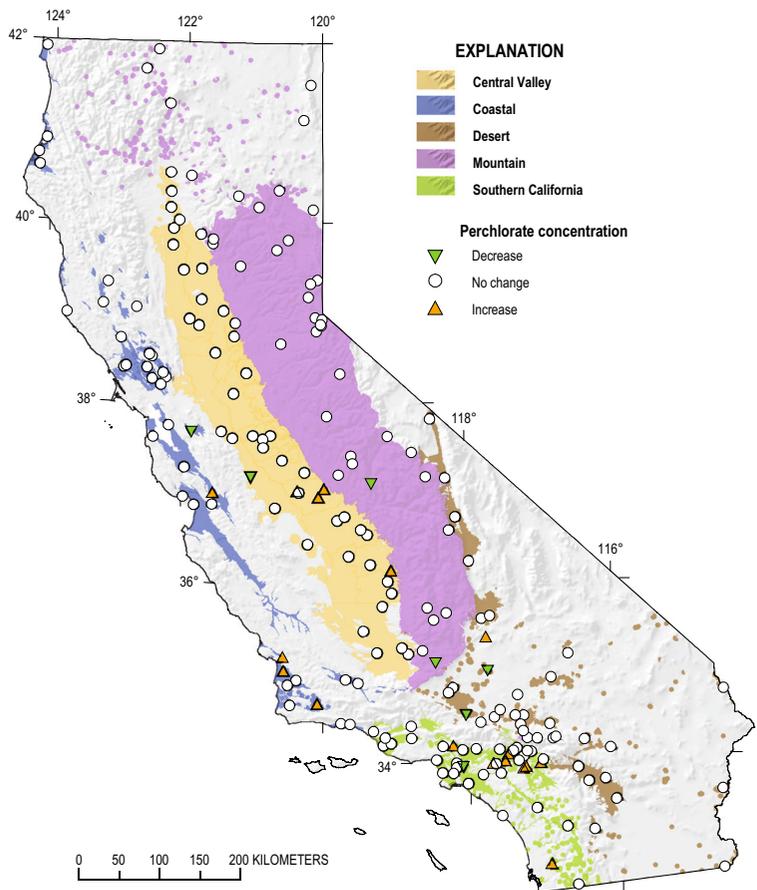
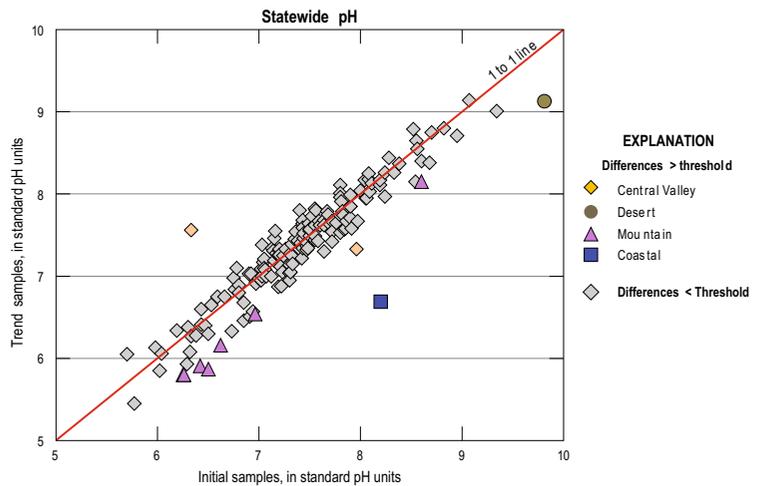


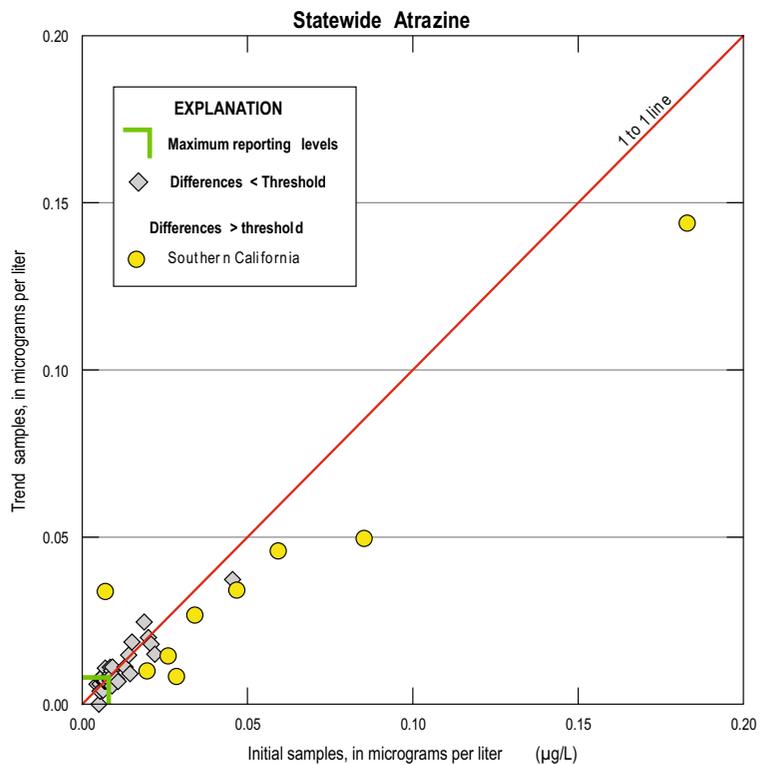
Fig. 6 Scatterplot of pH measured in initial vs. trend samples



<1 $\mu\text{g/L}$, there are nearly as many decreases (5) as increases (8). In contrast, for wells with concentrations >1 $\mu\text{g/L}$, there are many more increases (9) than decreases (2). When perchlorate is >1 $\mu\text{g/L}$ in California groundwater used for public supply, it is unlikely to have a natural source (Fram and Belitz 2011). It might be concluded, therefore, that the increasing perchlorate step trends observed here were occurring primarily in groundwater from wells with anthropogenic sources of

perchlorate. Ancillary observations consistent with this interpretation include the following. Perchlorate has been a groundwater contaminant of considerable concern in several parts of Southern California urban areas because of a long history of munitions manufacturing and historical application of fertilizers potentially containing perchlorate on citrus and other crops in some Southern California groundwater basins (Fram and Belitz 2011). Therefore, it is not unexpected that

Fig. 7 Scatterplot of atrazine concentrations measured in initial vs. trend samples



increasing trends in perchlorate would be detected in some deep wells used for public supply in Southern California. The wells with significant increases statewide primarily either occur in Southern California urban basins or in agricultural areas of the state such as the Central Valley or coastal basins where perchlorate-bearing fertilizers could have been applied in the past (Fig. 5). Significant differences among trend categories (increasing, decreasing, unchanging) were not found for perchlorate in relation to well depth, depth to the top perforation, categorical land use percentages, or age-dating variables (tritium and modern carbon) (Online Resource 7).

The decreasing step trend detected for dissolved oxygen in the Central Valley hydrogeologic zone may not indicate that concentrations of dissolved oxygen in California Central Valley groundwater are changing in any meaningful way. Changes in dissolved oxygen concentrations are most meaningful when they result in the groundwater going from oxic to anoxic or vice versa. McMahon and Chapelle (2008) defined anoxic groundwater as having a dissolved oxygen concentration less than 0.5 mg/L. Using this criterion, groundwater in 28 of the 224 trend wells was anoxic for both samples. Groundwater in 9 of the trend wells changed from oxic to anoxic between sampling periods, and groundwater in 8 of the trend wells changed from anoxic to oxic between sampling periods. No statistically significant relationships were found between dissolved oxygen trend categories (increasing, decreasing, unchanging) and any of the continuous well attribute variables evaluated in this study (Online Resource 7).

This study found that pH decreased statewide and in the Mountain hydrogeologic zone. The pH of most samples collected for this study was also measured by the NWQL, and it should be noted that trend evaluation of laboratory-measured pH data found increasing step trends statewide and in the Central Valley hydrogeologic zone. However, the pH of a water sample can change significantly within hours or even minutes after sample collection as a result of degassing, mineral precipitation, temperature change, and other chemical, physical, or biological reactions (U.S. Geological Survey 2006). Therefore, the field-measured pH values evaluated here should be considered most representative of aquifer conditions. The Kruskal-Wallis test results (Online Resource 7) indicated relationships between pH trend categories and two evaluated well attributes: depth to the top perforation in the well, and land use surrounding the

wells. Wells with relatively shallow depth to their top perforation may be more likely to have decreasing pH. However, the Wilcoxon rank-sum test results could not specifically show a statistically significant difference in top perforation depths between wells with decreasing pH and those with increasing pH. The statistically significant Kruskal-Wallis test results with regard to land use and pH changes should be considered with caution. The results suggest that wells with groundwater with decreasing pH are more likely to have a higher percentage of natural land use and a lower percentage of urban land use around them than are wells with groundwater with increasing or unchanging pH. However, this may be a case of autocorrelation since 7 of the 10 wells with groundwater with decreasing pH were located in the Mountain hydrogeologic zones where natural land use is prevalent.

Step trends were found for seven trace elements: aluminum, beryllium, boron, cobalt, lead, lithium, and nickel. For aluminum and beryllium, step trends were observed on a statewide basis only and not for any individual hydrogeologic zone. For boron, lithium, and nickel, step trends were observed in just one hydrogeologic zone, and not on a statewide basis. Trace elements have been identified by the GAMA-PBP as the most prevalent class of contaminants in California's groundwater (Belitz et al. 2015). In most cases, the source of trace elements in groundwater is natural, although in some cases, trace elements can be mobilized in aquifers by human activity (Jurgens et al. 2010; Ayotte et al. 2011).

In this study, the observed step trends in trace elements occurred primarily at concentrations much smaller than drinking water benchmarks, which indicates that these changes have limited significance with respect to water quality. For example, the highest concentration of aluminum detected in a sample from a trend well during either sampling period was 30 $\mu\text{g/L}$. The USEPA has a Secondary Maximum Contaminant Level for esthetic qualities of drinking water of 50 $\mu\text{g/L}$ for aluminum. The health-based threshold for aluminum in drinking water is a California Maximum Contaminant Level of 1000 $\mu\text{g/L}$. Similarly, the U.S. Maximum Contaminant Level for beryllium (4 $\mu\text{g/L}$) is ten times greater than the concentration detected in trend wells. The U.S. Action Level for lead (15 $\mu\text{g/L}$) is nearly twice the concentration detected in any trend well sample, and the California Maximum Contaminant Level for nickel (100 $\mu\text{g/L}$) is nearly ten times that of any trend well

sample concentration. Among the trace elements for which step trends were found, only boron was detected at a concentration greater than its drinking water benchmark, a California Notification Level of 1000 µg/L. Cobalt and lithium have no drinking water benchmarks; their maximum concentrations in samples from trend wells were 0.4 and 10 µg/L, respectively. Finally, the decreasing step trend for cobalt in the Central Valley hydrogeologic zone was based on an evaluation of only 9 wells and therefore merits skepticism.

Statistically significant relationships between constituent trend categories (increasing, decreasing, unchanging) and the evaluated continuous well attribute variables (Online Resource 7) were found only for nickel. Wells in which groundwater nickel is decreasing are more likely to have a higher percentage of urban land use around them than are wells in which groundwater nickel is increasing or unchanging. Likewise, wells in which groundwater nickel is increasing are more likely to have a higher percentage of natural land use around them than are wells in which groundwater nickel is decreasing or unchanging. It should be reiterated that all nickel concentrations measured in trend wells during both sampling periods were small (maximum 12 µg/L) relative to the California Maximum Contaminant Level (100 µg/L).

In this study, no step trends were detected for the 85 volatile organic compounds analyzed, and step trends were detected for only two of the 81 pesticide compounds. When these organic compounds are detected in California aquifers used for public supply, they are generally detected at concentrations near the reporting limits applied by the NWQL. In addition, the NWQL often reports estimated concentrations less than the effective reporting limits for these compounds. As a consequence, the threshold requirement applied in the present study, which screens out differences that are small relative to reporting limits, makes it difficult to detect step trends. Nevertheless, decreasing step trends were detected for atrazine statewide and for both atrazine and simazine in the Southern California hydrogeologic zone. Significant differences among trend categories (increasing, decreasing, unchanging) were not found for atrazine or simazine with relationship to the evaluated continuous well attribute variables (Online Resource 7). The most likely explanation for the observed decreasing step trends in atrazine and simazine in the Southern California hydrogeologic zone is that use of these herbicides within this zone has declined over

time. The California Department of Pesticide Regulation provides pesticide use statistics for California counties dating back to 1989 (<http://www.cdpr.ca.gov/>). Atrazine use in the 5 Southern California counties included in the Southern California hydrogeologic zone—Los Angeles, Orange, Riverside, San Bernardino, San Diego, and Ventura—declined from more than 5000 lb in 1989 to 315 lb in 2014. Similarly, simazine use in those five counties declined from more than 70,000 lb in 1989 to less than 17,000 lb in 2014.

An alternative approach used by Bexfield (2008), Barlow et al. (2012), and other researchers, assigns a uniform concentration value less than the lowest detected concentration to all results not detected by the laboratory. While this approach overcomes difficulties associated with variable laboratory reporting limits, it may exaggerate the true difference between paired results. The true concentration of a constituent whose result is censored by a relatively high reporting limit could actually be more similar to that reporting limit than to the value associated with the assigned lowest rank. Nevertheless, after applying the study methods previously described herein, the approach used by these researchers was additionally applied to the volatile organic and pesticide compound data in this study, and that approach yielded results very similar to those presented here.

Although step trends were detected for 17 constituents, statewide, or in one or more of the defined hydrogeologic zones, no effort was made to quantify the rates of change in concentration of these constituents based on just two sampling episodes nor were cause and effect relationships for the observed step trends explored in detail. The use of explanatory factors for statistical trend extrapolation relies on the assumption that the explanatory factors considered, such as land use, water resource management climate, and the dynamics of solute transport remain unchanged over time (Batlle Aguilar et al. 2007). For example, a fluctuating water table may exaggerate or mask changes in constituent concentrations (Pelayo and Evangelista 2003). A persistent drought was occurring in the State of California during the study period, which may have caused transient behavior in the observed concentrations of the evaluated water-quality constituents (Rousseau-Gueutin et al. 2013). The hydrogeologic mechanisms causing changes in water quality are complex and can vary in relation to the distribution and types of natural

and anthropogenic solute sources and geochemical conditions present.

This study found that step trends in groundwater quality can be detected after only 3 years. The expected observation of decreasing step trends for tritium statewide, and in nearly all of the hydrogeologic zones, demonstrated the utility of this method. However, not all step trend findings are relevant for water resource management. The magnitude changes observed in this study for dissolved oxygen in the Central Valley hydrogeologic zone, and for seven trace elements in one or more hydrogeologic zones, were not environmentally meaningful. Nevertheless, these patterns and identification of increasing step trends for orthophosphate, statewide, and in three hydrogeologic zones, along with the detection of decreasing step trends for atrazine and simazine in the Southern California hydrogeologic zone, provide early awareness to state and local water resource managers of changes to continue to evaluate through future monitoring.

In January 2014, the GAMA-PBP began a new undertaking of trend sampling, including additional sampling from the same trend wells used in the present analysis. During the new undertaking, a greater number (approximately 20 %) of the 1685 original status wells are being sampled for trends, with the goal of identifying more clearly regional groundwater-quality temporal trends in the State of California based on data from a larger number of wells and over longer periods of time.

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